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THE CONCEPTION AND ELECTROCHEMICAL STUDY OF AN ELEMENTARY MODEL OF A POROUS, TRIPLE-CONTACT ELECTRODE 2#

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ELECTROCHEMISTRY. The Conception and Electrochemical Study of an Elementary Model of a Porous, Triple-Contact Electrode

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ABSTRACT

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The characteristics of a monotubular electrode are defined so that it may serve as an elementary model of a porous, triple-contact electrode, and its application is described. An electrochemical study of this model made possible by the use of X-rays shows the influence of polarization on the interfacial properties of the system $Ag/KOH/O_2$. Author

Porous electrodes, particularly those referred to as the triple-contact type used currently in fuel cells, are characterized by a complex structure that does not permit an exact analysis of the process taking place within them. It is most probable, for example, that the performance of these electrodes is strongly influenced by capillary phenomena that are difficult to observe. At the same time, the interpretation of the results of electrochemical measurements can only be given with electrodes of well known geometric characteristics. Therefore, in order to attempt to explain the comportment of these electrodes, it is indispensable to have recourse to a simplified appropriate model that permits both a theoretical approach and experimental verifications.

If a particular macroscopic property of a porous body is examined, it is generally possible to determine its characteristics with sufficient approximation by making an orderly porous structure that will correspond to its own disorderly structure. In the simplest of cases, the former will be composed of a network of cylindrical pores of identical cross sections and orientation (Ref. 3). The diameter of a constituent canal of this network will be equal to the mean diameter of the pores of the initial structure; its length will be equal, for example, to the mean length developed in these pores.

The study of this model network can then lead easily to a study of one of its elements. However, since it is difficult to make a direct study of a tube of microscopic dimensions, a larger cylindrical electrode will generally be chosen (Refs. 1-5). If such a model embodies useful simplifications, it should reproduce the same phenomena that take place in the porous electrodes. Consequently, in the case of triple-contact electrodes, it is indispensable for the model to be sufficiently small not only for the mechanical effects of capillarity to be evident, but also, as in the micropores, for all the gas/electrolyte surface to be

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entirely subject to capillary forces. The meniscus obtained in this tube will then have the same form as that existing in the pores of considerably smaller diameter. Finally, the relation between length and diameter in the model should be similar to that existing in the ordered network.

It does not appear that the models of triple-contact electrodes used thus far by certain authors (Refs. 4-6) have fulfilled these conditions. This is doubtless essentially because of the difficulty in observing the position and form of the meniscus in the metallic capillary tube. It has been indicated recently (Ref. 7) that the X-ray was a great aid in the study of porous electrodes. In this Note, we show that by observing the position and form of the meniscus, this technique permits the study of the model electrodes previously defined. However, X-ray pictures with the amount of contrast needed to show clearly the limits of separation of the three phases in their occurrence can be obtained only if certain experimental conditions are fulfilled. In particular, taking into account the absorption of rays in the electrolytic phase and in the metallic walls through which they pass, the thickness of the latter should never exceed a few microns. /2

Of course, such thin tubes cannot be prepared by the usual manufacturing processes. The only way to make them is by depositing a thin metallic layer on the internal wall of a supporting tube permitting passage of X-rays. In the study described as an example in this Note, capillary electrodes of silver were deposited by chemical means.

The capillary tubes chosen as support are made of drawn glass. Selection on the basis of dimension makes it possible to retain only perfectly cylindrical samples. Their internal diameter is 0.2 mm, their length 50 mm, and their wall thickness is not over 0.1 mm. The deposit of silver adheres perfectly to the supporting tube, its thickness being of the order of a few microns and its surface relatively rough but without marked discontinuities. Its resistance as measured at the ends of the tube is not greater than a few tenths of an ohm.

The electrolytic cell that was used (Figure 1) is composed of two compartments united by the capillary tube. The lower compartment is filled with a solution of KOH 5_N and contains a counter-electrode and a comparison electrode. The upper compartment communicates with a reservoir of oxygen that makes it possible to maintain the level of the electrolyte within the range of observation. The tests are made at a temperature of about $20^{\circ}C$.

With the aid of a potentiostat, we have been able to cause a variation in the polarization by successive stages in the direction of the cathode and then in that of the anode. The duration of each stage was about 2 minutes, which allowed a stable state to be established, during

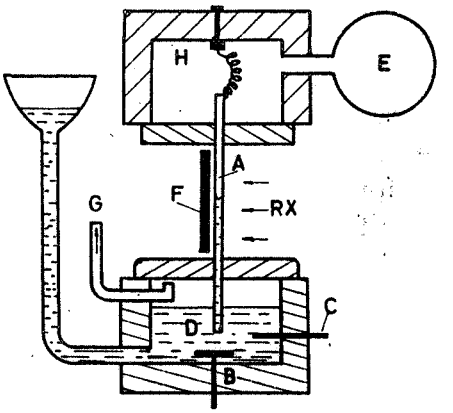

Figure 1. Electrolytic cell.
A, capillary electrode; B, counter-electrode; C, comparison electrode; D, electrolyte; E, gas reservoir; F, photosensitive film; G, vent tube; H, contact of the capillary electrode

which the pictures were taken. The X-ray photographs obtained show important variations in the angle of contact of the meniscus with the wall.

Diagrams have been prepared showing the variations in the angle of contact as a function of the tension of the electrode. A characteristic curve is shown in Figure 2. It is distinguished by the presence of a sharply defined maximum in the anodic area (E_h at about +300 mv) and a portion of parabolic form in the cathodic area. The latter contains a minimum situated systematically between E_h = -50 mv and E_h = -150 mv. /3

We should mention, finally, that for strong cathodic polarizations (E_h < -0.5 v approx.), the dispersion of the angular values increases considerably.

The separations found in the measured values of the angle of contact are translated undoubtedly in a variation of the interfacial tension between solid and liquid, since the interfacial tensions between solid and gas, and between liquid and gas, can be considered constant according to our experiments. This variation can be explained in part by the intervention of electrocapillary phenomena, and in part by a possible modification in the structure of the interphase region, particularly in its solid part. As a matter of fact, different oxides that do not necessarily have the same interfacial tension can be formed successively at the time of the anodic polarization of silver.

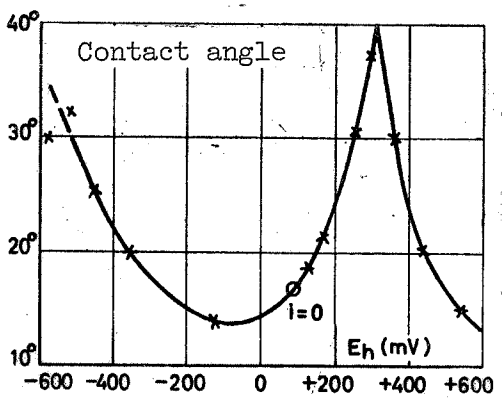

Figure 2. Variation of the angle of contact of the meniscus with the wall as a function of the polarization, using a monotubular silver electrode

Referring to the tension-pH diagram (Ref. 8), it is possible, moreover, that only the metallic silver is stable in the cathodic area. However, we believe it probable that in the presence of oxygen a deposit of oxide or of chemically absorbed oxygen may exist on the surface, even in the case of relatively negative tensions. This deposit and its structure /4 may vary without doubt as a function of the potential; it is probable, therefore, that the interfacial tension between solid and liquid will not be constant here either.

The electrocapillary phenomena must certainly take place, but it would be difficult for them alone to account for the observed effects. As a matter of fact, if the maximum encountered for E_h = +300 mv can be considered rigorously as a maximum electrocapillary even though the curve in this region is very different from a parabole, the increase of the observed interfacial tension for strong cathodic polarizations could only be explained by a possible adsorption of a new variety for which no hypothesis can be put forward.

In conclusion, through the observation of changes in the geometric characteristics of the system, this study shows the variation in interfacial tension between solid and liquid as a function of the polarization of the electrode. The method described here provides, therefore, a means of studying phenomena impossible to observe up to now but that, nevertheless, can be the controlling factor in some cases in the operation of porous triple-contact electrodes.

Proceedings of the Academy of Science of Paris, Volume 257, pp. 3394-3397 (25 November 1963).

References

1. Daniel-Bek, V. S. Zh. Fiz Khim, 22, p. 696, 1948.
2. Ksenzhek, O. S. and Stender, V. V. Zh. Fiz. Khim, 31, p. 117, 1957.
3. Winsel, A. Z. Electrochem., 66, p. 287, 1962.
4. Will, F. G. J. Electrochem. Soc., 110, pp. 145 and 152, 1963.
5. Weber, H. C., Meisnner, H. P., and Sama, D. A. J. Electrochem. Soc., 109, p. 884, 1962.
6. Palous, S. and Buvet, R. Bull. Soc. Chim. Fr., p. 1602, 1962.
7. Bonnemay, M., Bronoël, G., and Levart, E. Paper read at the September 1962 meeting in Boston of the Electrochemical Society.
8. Pourbaix, M. Atlas d'equilibres electrochimiques a 25°C. (Atlas of Electrochemical Equilibriums at 25°C) Gauthier-Villars, Paris, p. 398, 1963.

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